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## STRUCTURAL AND TECHNOLOGICAL PARTICULARS OF GLASS MELTS

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Works on the structure of silicate and glass melts are reviewed using the principles of synergetics and the concepts of a cluster and fractal. Some particulars of commercial technological processes and the operational reliability of manufactured articles are examined.

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**Key words:** clusters, synergetics, fractals, structure of melts, technological processes, nanotechnologies, glass strength.

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Glass melts play a fundamental role in the technology used to manufacture diverse glass articles. At the same time not enough attention is devoted in the scientific-technical literature to the structure and technological characteristics of melts and their interrelation, especially in connection with the development of comparatively new interdisciplinary scientific directions: synergetics, fractal analysis and nanotechnologies [1–3].

The term **synergetics** was proposed at the beginning of the 1970s by H. Haken. Synergetics studies the processes involved in self-organization in nonequilibrium systems which consist of several or many identical or dissimilar parts interacting with one another and in which spatial, temporal, spatio-temporal or functional structures arise.

Synergetics is the fundamental basis for the concept of **fractals** (self-similar structures). This term was introduced in 1975 by B. Mandelbrot. The range of scales where fractal structures are observed extends from interatomic distances in matter to the distances between clusters of galaxies in the Universe. This suggests that any sufficiently strong irregularities in nature and technology strive to acquire a fractal structure.

The term **nanotechnologies** refers to a collection of technological methods and techniques used to study, design and produce materials, setups and systems (with dimensions 100 nm and smaller) that engender improvements in and additional performance and/or user characteristics of finished products.

A considerable number of scientific publications in diverse fields of knowledge are devoted to these directions.

The basic principles of the scientific directions enumerated above are fully applicable to silicate melts. Specifically, the fractal basis of melts can be formed by self-organization of single nanostructural elements (clusters).

We shall examine some structural features of melts in accordance with cluster and fractal concepts and in conjunction with technological processes in the manufacture of glass products. The principles of nanotechnologies in conjunction with glass technology are expounded in [4].

**Structural Particulars of Silicate Melts.** Studies of the structure silicate melts are of considerable interest for geochemistry (magmatic melts), metallurgy (slag melts) and silicate technology (glass and enamel melts, binding melts in the manufacture of refractories, ceramics and so forth). There is considerable research on different structural aspects of silicate melts. Research up to 1988 is systematized in [5–10].

Melts are a kind of liquid state, basic models of which were proposed in 1927–1961. The following models have received the greatest recognition: cybotaxic (G. Stewart, 1917), lattice (D. Lennard-Jones, 1937), hole (Ya. I. Frenkel', 1945) and defect-free (J. Bernal, 1961).

W. Weyl and E. Marboe have analyzed the basic structural models of simple and complex liquids in application to glass formation processes [11]. They divided all liquids, including melts, into three groups corresponding to three structural models: Bernal, Frenkel' and Stewart.

A generalized classification of liquids (melts) is proposed in [7]:

- by the type of basic structural elements: molecular, ionic, metallic (atomic) and network (predominately chain, layer and framework covalent structures);

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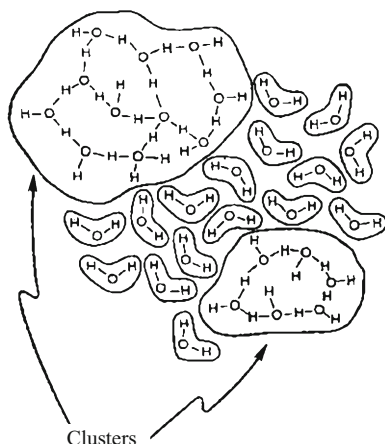


Fig. 1. Schematic diagram of the cluster model of water.

— by the correlation with initial crystal lattices: with one — quasi-crystalline, with several — hybrid, or conglomerate; in absence of a correlation — anti-crystalline.

All models listed above can be classified as quasi-crystalline, but the cybotaxic model is more convenient for complex multi-component melts. This is the model that has undergone the greatest elaboration in recent years. In the process the terminology has changed. The synonymous term clusters is now used almost exclusively for the terms cybotaxic groups and cybotaxes.

**Clusters in Melts.** The basic principles of the cybotaxic model of a liquid which have been presented above also hold for cluster models and their different forms (quasi-crystalline, quasichemical and others).

It is proposed in [7] that in a complex melt clusters of different types float in a more disordered, not closely packed, liquid with quasi-gas structure. Ultimately, a complex melt should be described as a conglomerate of zones of different structure that occupy fractions of the total volume. The clusters and the disordered zone are thermodynamically unstable systems: the partial Gibbs energy for clusters is higher and that of the disordered zone lower than the average value for the entire melt. This determines the dynamism of the melt structure: clusters and the quasi-ordered zone continually exchange structural units because of energy fluctuations. However, the lifetime of the clusters is still long compared with that of the thermal fluctuations in the melt as well as the duration of elementary acts of viscous flow, diffusion, heat conduction and other processes determining the kinetic characteristics of a melt. For multi-component melts the energy nonequivalence of interatomic interactions of different types is responsible for the appearance of clusters with different structure, composition and temporal stability. The most strongly interacting components form the most stable and long-lived clusters. The ratio of the volumes occupied by clusters and the disordered zone is determined by the temperature of the melt. As temperature increases the cluster frac-

tion and cluster sizes decrease while the disordered zone fraction increases.

The fruitfulness of the cluster approach to studying liquids and melts is examined in a number of monographs [7, 12, 13]. Cluster models are also fruitful in research and development work on nanotechnologies [14].

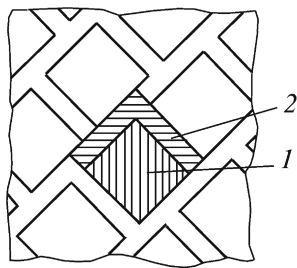
A classical example of a cluster model for molecular liquids is water (melted ice). Liquid water comprises a conglomerate of large tetrahedral associates of water molecules  $H_2O$ , forming and decomposing (flickering clusters). A schematic diagram of the cluster model of water is displayed in Fig. 1 [7]. According to the cluster model, ice-like formations are present in water even before the first stable ice crystals form [15].

Cluster models have been used to study metallic melts. A number of authors have observed jumps in the polytherms of different properties. To explain the mechanism of structural transformations in liquids it has been suggested that cluster polymorphism phenomena (polymorphic transformations in ordered micro-groups of a liquid with crystal-like packing of the atoms — clusters) exist in liquids [16].

The structure of silicate melts is much more complicated than that of atomic (metallic) and ionic (salt) melts. Even though there are different viewpoints concerning these questions most researchers are of the opinion that silicate melts are nano- and micro-nonuniform dissociated liquids in which there are no molecules of free oxides and no nondissociated compounds. Silicate structures are built in a different manner by a combined collection of  $[SiO_4]$  tetrahedra forming anionic coordination spheres of cations. For this reason, in order for one or another phase to crystallize anionic fragments with an appropriate configuration must be present in melt in the required amount, determined not only by the cation concentration but also by the predominate arrangement of the cations relative to the dominant anionic groupings.

Nonequilibrium metastable states genetically related with the structure of the initial solid phases are characteristic for multi-component silicate melts. Here, hysteresis of the properties as a function of temperature as well as a dependence of the structure and properties of melt on the temperature and aging time, rate of temperature change and impurity content are often observed.

One simple model of silicate melts is the two-lattice model. According to this model melts are divided into network-forming ( $Si^{4+}$ ,  $Al^{3+}$  and others) and modifying ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and others) depending on the role of cations in the structure. The former form and enlarge cluster groupings while the latter participate in their destruction. The primary magmatic silicate melts possess a complex variable structure determined by many diverse factors. This makes it difficult to build thermodynamic models of such systems. Many researchers have gone down the path of building semi-empirical models employing the concentrations of the components in phases of the system and simplified variants of the melt structure; mineral phases are treated as ideal solutions. Data on magmatic silicate melts are generalized in [17].

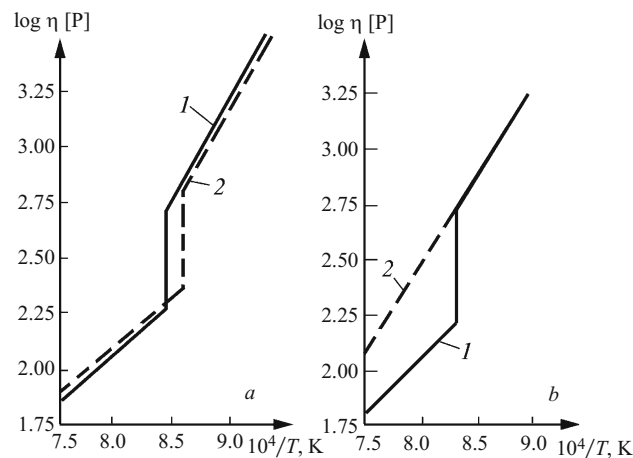


**Fig. 2.** Two-dimensional model of micro non-uniform structure of glass: 1) structural complex; 2) micro region of weakened structure.

In the physics and chemistry of glass conclusions are drawn on the basis of studies of the structure of solid glasses, which are treated as frozen melts. This has been confirmed experimentally for a number of simple glasses. Definite conclusions about the structure of melts are drawn on the basis of high-temperature measurements of structurally sensitive properties (viscosity, electric conductivity and so forth). Information on the relationship between the properties and structure of glasses and melts is contained in [10].

Various researchers studying the structure of glasses have attempted to identify the main structural units associated with deformations and relaxation phenomena. G. K. Demishev developed the concept of heterodynamism of silicate glasses as a supplement to existing ideas about the micro non-uniform structure of glasses, underscoring the presence of chemically nonuniform regions of submicron size in their structure and presupposing different mobility for individual structural elements [18, 19]. In this case the main structural element of glass is a structural complex (cluster) in the form of a local region of strong bonds (for example, ionic-covalent) where a definite degree of ordering is assumed to be present.

G. K. Demishev also proposed a two-dimensional model of a micro-nonuniform structure of inorganic structures (Fig. 2). This model consists of micro nonuniform regions (structural complexes) conjoined by an interlayer where the interatomic interactions are of a different nature from those in the complex itself. Each complex 1 forms together with adjoining sections of the interlayer 2 an elementary cell and the entire model is comprised of the corresponding articulations. The properties of an elementary cell are assumed to be identical to those of the entire model. The structural complex interacts with surroundings comprised of similar complexes via intermediate, less ordered (or completely disordered) regions of weak and overstressed bonds. Since these and boundary regions are the weakest spots according to the energy data, they determine the initial behavior of glasses under different loads. D. K. Demishev's model is, essentially, a cluster model and reflects the micro nonuniform structure of glass as well as glass-forming melts, taking account of the particulars of technological processes in the glass industry.



**Fig. 3.** Temperature dependence of the viscosity for melts in the system  $\text{Na}_2\text{O-PbO-SiO}_2$  with compositions 1 (a) and 2 (b) in direct (1) and reverse (2) experiments (1 P = 0.1 Pa · sec).

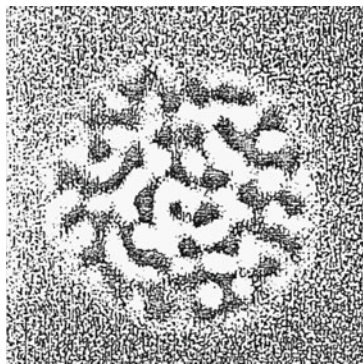
The phenomenon of cluster polymorphism in metallic melts was mentioned above. The results of studies of silicate melts in the system  $\text{Na}_2\text{O-PbO-SiO}_2$  (Table 1), including measurements of the viscosity with a resonance vibratory viscosimeter, are presented in [16]. Structural transitions, manifested as an abrupt change of the viscosity and activation energy of viscous flow, were found for a number of melts. The effects observed are explained by the phenomenon of polymorphic transformations in clusters of the compound  $\text{Na}_2\text{O} \cdot 3\text{PbO} \cdot 6\text{SiO}_2$  (Fig. 3).

The results of the experimental and theoretical studies of the thermodynamics and physical-chemical properties of silicate melts, including some forms of glass, are generalized in [20]. Data obtained by modern physical methods, including the direct method of high-temperature Raman spectroscopy, on the structure of silicate systems are presented. It is concluded on the basis of the experimental data obtained by this method that the structure is a globular (cluster) construct of simple high-silica silicate melts; the base of such melts is comprised of spherical ions with fused-silica structure; the surface layer of these anions consists of  $\text{SiO}_4$  tetrahedra of the discrete type with one non-bridge oxygen per tetrahedron.

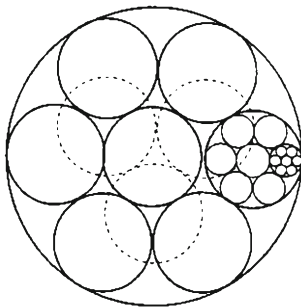
The relations between the details of small-angle x-ray or neutron scattering and the medium-range order in glass were

**TABLE 1.** Compositions of Melts in the System  $\text{Na}_2\text{O-PbO-SiO}_2$

Molar composition of melts, %		
$\text{SiO}_2$	$\text{PbO}$	$\text{Na}_2\text{O}$
64	27	9
64	25	11
64	20	16
60	20	20
65	15	20



**Fig. 4.** Frozen fluctuations of the atomic density for glassy  $\text{SiO}_2$  according to data from neutron scattering and high-resolution electron microscopy.



**Fig. 5.** Fractal-geometric evaluation of the structure for spherical particles.

studied in [21]. The author showed that frozen density fluctuations — micelles (clusters) — are 1 – 1.5 nm in size (Fig. 4). The author also established that to a first approximation the nature of the medium-range order in glasses can be easily ascertained on the basis of reliable data on medium-range order in crystals. The corresponding experimental data are presented for glasses and halide melts and calculations are presented for crystals with the corresponding compositions.

For colloidal coloring the composition of glass and the temperature conditions promote self-organization of metal ions in glass melt in clusters and right up to the formation of crystal embryos (centers of crystallization) [22].

**Fractals.** Geometric objects (lines, surfaces, three-dimensional bodies) possessing the property of self-similarity and often having a strongly indented surface are said to be fractals. Self-similarity as a fundamental property of a fractal means that the fractal is a more or less unitarily organized structure in a wide range of scales. For example, under magnification small fragments of a fractal are found to be very similar to large fragments of the same fractal. Many fractals encountered in nature and technology (fracture surfaces of rocks, metals, ceramics, glass, clouds, tree roots, coast lines, turbulent flows, foam, gels, elements of snow flakes, frosty pattern on glass and so on) have no precise geometric simi-

larity, but they do reproduce in each fragment the statistical properties of the whole. It is not for nothing that nature prefers fractal forms. This is because such forms are obtained by simple multiplication and changing the dimensions of some elementary structural block.

For fractals the disordered structure of particle aggregates (clusters) can be evaluated in terms of their fractal parameters. For example, a very simple fractal-geometric evaluation for spherical particles (Fig. 5) is presented in [23] where the process of gel formation is analyzed.

The basic relation in fractal theory is the relation between the mass  $M$  of a fractal aggregate and its characteristic size  $R$  (often, the radius of the aggregated is used as the latter):

$$M = aR^D, \quad (1)$$

where  $D$  is the fractal dimension, making it possible to evaluate the occupancy of a definite space by aggregated particles. For the example considered  $D = \log 13 / \log 3 = 2.33$ . A value  $D < 3$  indicates that the void fraction in the volume increases as the radius  $R$  of the fractal increases.

The number  $N$  of particles in an aggregate is related with its radius by the expression

$$N \sim (R/r)^D, \quad (2)$$

where  $r$  is the radius of the particles in an aggregate with radius  $R$ .

The relations presented can be used in fractal analysis of structures with spherical particles. An example is precious opal, which is comprised of closely packed spherical  $\text{SiO}_2$  nano- and microparticles. The fractal structures formed in real systems usually have a quite complex structure so that they cannot be described by means of simple geometric relations; quite complex mathematical functions are used.

The fractal exponent for disordered structures can be obtained by determining the average size (or radius of gyration) of statistically similar aggregates. More complex fractal structures where the property of self-similarity is manifested only in a definite direction in space as well as surface fractals formed in a surface layer of the particles exist. The prevalence of fractals in nature has already been mentioned above.

Natural aluminum-silicate rocks (clays) possess elements of fractal structure due to sheeting, porosity and presence of chemically and physically bound water. When clayey materials are wetted water penetrates into the space between the layers and fills the pores, causing swelling; the layers acquire the ability to easily move relative to one another. On drying (without the use of special additives) clays are capable of forming a network of cracks which exhibits a sharply expressed fractal character, reflecting structural particularities (Fig. 6). Two levels of self-similarity can be seen in the figure; but, if the conditions of drying change, then a larger number of fractal levels can be obtained.



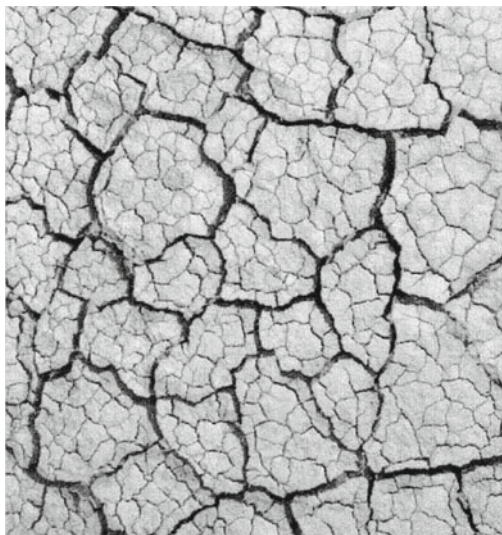


Fig. 6. Fractal system of cracks arising when clay suspensions dry.

A diagram showing successive formation of a three-dimensional gel structure of alumina from a colloidal solution is displayed in Fig. 7 [24]. As one can see from this figure the initial stage of the formation of micro-gel is an aggregation of separate colloidal particles in short chains (fractal clusters). As the lengths of the chains increase the colloidal particles start to attach not only to the ends but also the sides of the chains. In this way branching chains cover a spatial region but without interfaces being formed (micro-gel region). As the gel-formation process develops each individual spatial region of the micro-gel increases in size by attachment of new sol particles. In the process interfaces form, and viscosity increases. The gel structures which arise propagate in the region of surrounding liquid until the gel phase occupies the entire volume. The gel formed in this manner possesses a sharply expressed structure.

Fractal ideas were also used to study the structure of simple glasses [21]. It was shown on the basis of a fractal analysis performed by the author that the structures formed in alkali and alkali-earth silicate glasses are mainly two-dimensional, more precisely, their fractal dimension is fractional, as the diffuseness of the planar image attests (see Fig. 4).

The interrelation of nanotechnologies and the principles of synergetics and fractal analysis should be noted. This interrelation is examined in [25], which is devoted to studies of catalytic processes in polymer nanosystems, which, in the opinion of the authors makes it possible to synthesize polymer nanocomposites directly during the polymerization process. The modern concepts of synergetics, fractal analysis and irreversible-aggregation and other models were used to study these processes. Fractal analysis of processes, specifically, chemical reactions, makes it possible to determine the fractal dimension of the particles formed and to use it as a structural parameter characterizing the configuration of a particle and the arrangement of its elements in space. The re-

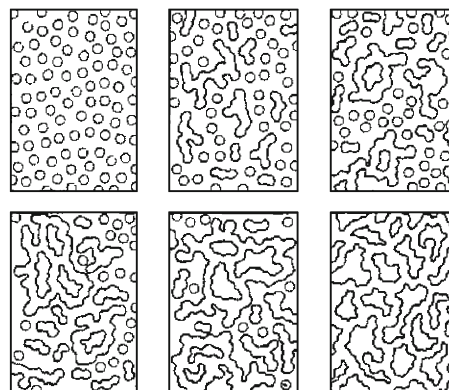


Fig. 7. Diagram of the sequence of formation of a volume gel structure of  $\text{SiO}_2$  from a colloidal solution.

sults of fractal analysis based on data on the kinetics of reactions in polymers are studied using experimental data and the general fractal equation

$$Q \sim \tau^{(3-D_f)/2} \quad \text{or} \quad \log \tau \sim [(3 - D_f)/2] \log \tau, \quad (3)$$

where  $Q$  is the degree of conversion (completeness) of a reaction,  $\tau$  is the time and  $D_f$  is the fractal dimension.

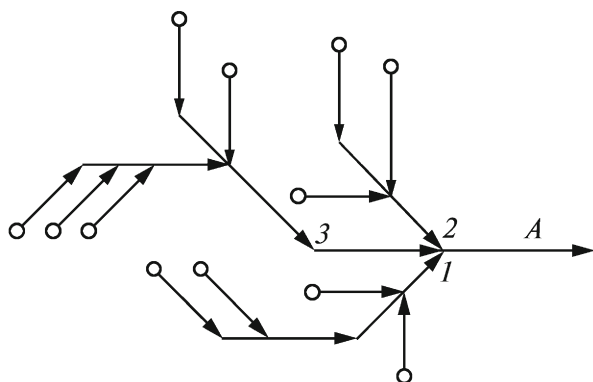
### Technological Processes with the Participation of Glass Melts

Melts of commercial glasses are usually multicomponent (quartz glass is an exception) and are obtained in glass-making furnaces at the time batch is melted. The following stages occur in the volume of the melt: silicate formation, glass formation, fining and homogenization. Technologically uniform but structurally nonuniform glass melts are obtained during normal fining. The technological processes of formation and heat-treatment follow; many types of articles undergo cold processing and decoration.

In any manufacturing process the technological processes are conducted using appropriate equipment. A technological process together with its equipment can be termed a technical system (TS). The processes occurring in technical systems have a distinct fractal structure. The structure of the minimal technical system presumes that two types of processes occurring in the TS — primary and enabling; this division is relative. Any process can be primary with respect to enabling processes, while any enabling process can be regarded as primary with respect to “its own” enabling processes.

An approximate technological scheme for obtaining glass-forming melt in a glassmaking furnace is shown in Fig. 8. The circles in the diagram denote technological operations and physical-chemical phenomena required for the enabling processes.

A primary process incorporates three enabling processes which are primary or the corresponding technological operations and physical-chemical phenomena. For example, the



**Fig. 8.** Technological scheme of the process of obtaining glass-forming melt in a glassmaking furnace: *A*) primary process; 1, 2, 3) enabling processes: 1) combustion of fuel in the glassmaking furnace; 2) batch and cullet preparation and loading into the glassmaking furnace; 3) interactions in the batch and melt.

process 1 requires input of fuel and heated air and combustion of fuel and heating of the batch and cullet; process 2 involves batch and cullet preparation, batch and cullet loading into the furnace and primary heating of the batch and cullet in the doghouse; process 3 involves the technical stages of melting and glassmaking (silicate and glass formation, fining and homogenization) as well as physical-chemical phenomena (chemical interactions, transport and surface phenomena).

**Glassmaking.** In glassmaking complex physical-chemical interaction processes occur in melts, flickering clusters appear, and nano- and microstructural nonuniformities form in the glass-forming melts. These melts are complicated disordered and nonequilibrium systems. According to the basic principles of synergetics, in such systems the relative independence of separate elements of the system is secondary to the corporate behavior of these elements: near equilibrium an element interacts only with its nearest neighbors, far from equilibrium an element sees the entire system as a whole and the degree of coordination in the behavior of the elements increases — self-organization occurs, its fundamental principle being the appearance of a new order and increasing complexity of the system through fluctuations of the states of the elements and corresponding systems. Under these conditions self-organizing fractal structures of the melt form; their driving force is the tendency of the system to decrease free energy. The unitary structural elements forming the fractal structure of the melt are fractal clusters, which have been found in melts of metals, polymers and silicates [16, 25].

**Crystallization** of molten glass can occur in commercial glassmaking furnaces; this is associated with the appearance of flaws during the manufacture of the largest articles (sheet glass, glass containers, houseware and others). The nucleation and growth of a crystalline phase in melt proceeds according to the following scheme:

clusters (melt) → crystal embryos → crystals (solid phase).

The theoretical underpinnings of crystallization processes, including in glass, have been worked out quite well and are elucidated in the works of many researchers.

Crystals appear primarily in the stagnant zones of glassmaking furnaces, contact layers at boundaries with refractories, cords, nondissolved quartz grains and elsewhere. Mass crystallization in the melt tank can occur in emergency situations, when glass outflow stops and the temperature of the molten glass decreases to the crystallization temperature (about 100 – 1200°C). The character and diagnostics of the crystal flaws are described in detail in [27].

It should be noted that the experience gained in manufacturing plants at home and abroad shows that the correct choice of glass composition, efficient glass furnace design, optimal process regimes and high-quality refractories make it possible to obtain high-quality glass with virtually no crystal flaws over a long service period of the glassmaking furnace.

**Forming.** Glass and glassware forming begins after the glass melt has been prepared, in the course of which the melt temperature is lowered to secure the viscosity required for forming. During forming of glass and glass articles the surface cools rapidly, which inevitably results in the appearance of a loosened surface layer [28]. The formation of such a layer and high thermoelastic stresses during forming gives rise to the appearance of nano- and microcracks in the layer, whose network has a fractal character and to a certain extent reflects the structure of this layer. The ion-exchange method, used by F. M. Ernsberger [29] to detect such cracks, serves to confirm this.

The determining factor in the forming of glass articles is the rate of solidification of the glass, which is determined by the viscosity changes as a function of the temperature and the temperature changes as a function of time. In the process high-viscosity molten glass cools and solidifies as a result of complex heat exchange with the surrounding medium with participation of heat conduction and radiation. The character of the solidification of glass during forming is examined in detail in [30].

The following particularities of commercial forming should be kept in mind:

1) the high-viscosity molten glass going into the forming process is not completely chemically, thermally and optically uniform;

2) the molten glass is cooled non-uniformly; this especially concerns forming with the use of molds, when the high-viscosity molten glass touches the heat-removing surface at a limited number of points;

3) cooling and solidification of the molten glass start from the surface and propagate into the interior of the glass.

Considering these particulars of the molten glass and its cooling conditions it can be asserted that viscosity changes will be fragmentary on the surface (rapid process) and in the interior (slow process).

A number of studies have shown that a grainy structure with 4 – 8 μm “grains” (parallel to the forming surfaces) is

fixed during the forming period. However, the transverse sections of the formed articles (perpendicular to the forming surfaces) have a layered structure with layers of approximate thickness  $2 - 4 \mu\text{m}$ .

Thus, the glass solidification process during forming can be imagined to occur in two stages:

- the appearance of “solidification nuclei” (local regions of glass with elevated viscosity) and formation of a solidification “layer”;
- the continuation of the “solidification layer” into the interior of the glass.

The formation of “solidification nuclei” is a surface process; the rate of solidification (change of viscosity in time) is proportional to the number of “solidification nuclei” and the viscosity gradient:

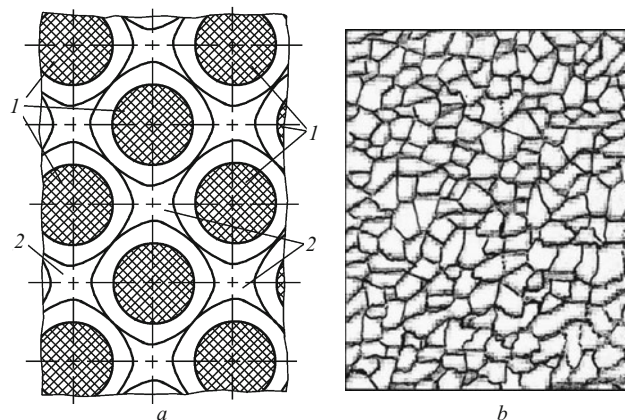
$$d\eta/d\tau = kN\Delta\eta, \quad (4)$$

where  $\eta$  is the viscosity,  $\tau$  is the time,  $N$  is the number of “solidification nuclei,”  $k$  is the coefficient of proportionality and  $\Delta\eta$  is the viscosity gradient.

The solution of this equation and its application to the forming process are examined in [30]. Fractal formations with their own articulation of elementary cells, similar to G. K. Demishev’s structural model examined above, arise in each “solidification layer.” Apparently, this explains the unpredictable character of the appearance of structural nano- and micro-defects and subsequently the development on their basis of main cracks under the action of thermoelastic stresses and mechanical loads.

**Heat Treatment.** Primarily two forms of heat treatment are used in the mass production of glass articles: annealing and tempering.

The considerable thermoelastic stresses which arise during forming undergo relaxation during **annealing**. According to data obtained by G. M. Bartenev and, et al. the relaxation processes occurring when glass articles are annealed have a distinct structural character [8]. Two relaxation processes are observed at temperatures below  $T_g$ :  $R_1$  and  $R_2$ , which are not associated equilibrium viscous flow. The relaxation process  $R_3$ , responsible for viscous flow, is practically not observed because of the low velocity in the annealing region; temperatures close to  $T_g$  are exceptions. The relaxation process  $R_1$  is supposed to be related with local deformations of the fluctuation network glass and the process  $R_2$  with the mobility of the micro-regions of the nonuniform structure of the glass — structural complexes (clusters). These conclusions are in qualitative agreement with the data from studies using the continuous spectrum and internal friction. Studies of the relaxation characteristics of alkali and low-alkali glasses have established that the contribution of the process  $R_2$  to stress relaxation during annealing is about 70 and 80%, while the contribution of the  $R_2$  process is only about 5%. It should be noted that in accordance with Fig. 2 the mobility of the structural complexes is due to the lower viscosity and higher mobility of the interlayers between the structural complexes. As



**Fig. 9.** Arrangement of zones of heat transfer (a) and the fracture character of tempered glass (b).

a result the thermoelastic stresses decrease to an admissible level.

During **tempering** glass articles are heated to a temperature determined approximately (and refined technologically) by G. M. Bartenev’s relation ( $t \sim t_g + 80^\circ\text{C}$ ). During the subsequent intense cooling the high-temperature structure becomes frozen in the surface layers of the glass articles and thermoelastic compression stresses much higher than the total strength of the articles are created. An arrangement on the surface of sheet glass of zones of strong (a) and weak (b) heat exchange using a multi-nozzle blowing lattice is presented in Fig. 9. The corresponding “imprints” on the surface of the glass can be seen by examining a sheet of tempered glass in partially polarized reflected light. The character of the fracture of tempered glass under external forces is also presented in the figure. It is evident that the hardening and fracturing of the glass are fragmentary. Tempering is most intense in the central part of the air stream. Zones of low strength, where fracture occurs under the corresponding loads, lie between zones of high strength. Taking account of the nonuniformities of the glass (at the nano- and micro-levels) the crack network develops nonuniformly but is fractal, similarly to crack formation in drying clayey suspensions (see Fig. 6).

**The performance reliability of glass articles** is largely determined by the melt properties. The uniformity of the molten glass, absence of flaws and optimal forming and heat treatment (annealing, tempering and ion-exchange hardening) conditions determine the primary performance indicator — the strength.

The basic characteristics of sheet glass and glass container manufacturing — the most common glass articles manufactured by the glass industry (more than 85 wt.%) — are presented in Table 2.

Better conditions for obtaining technologically uniform molten glass and forming articles with fewer surface and structural defects are created for sheet glass. This explains the high strength of sheet glass, especially when different



methods of hardening are used. It should be noted that glass is used for glazing in air- and spacecraft, where glass articles not only function as optical elements but also function as a structural material that is capable of bearing different loads and ensure both the reliability of the object and the safety of the crew.

An integral part of the work done to increase the operational reliability of glass is the study of how glass fractures. The theory of the thermal fluctuation nature of the fracturing of materials is examined in the review monograph [31].

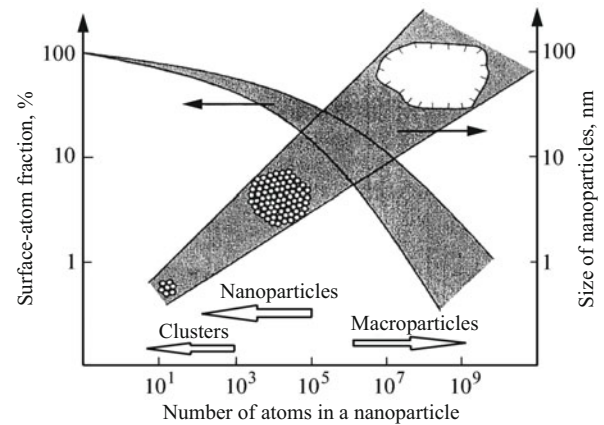
It is known that the fracturing of solids, including glass, is a process of multiple nucleation and development of nano- and microcracks. Nucleation, growth and aggregation of different kinds of nano- and microdefects appear during the fracture period, right up to the appearance of main cracks. Fracture is of a stochastic nature. The process of damage accumulation is itself self-similar; during the fracturing process only the dimensional parameters change while the non-dimensional characteristics of microdefects, for example, the form of the size distribution curve of their number, do not. For this reason, the machinery of the theory of sets of fractional dimension — fractals — has come into use in recent years [32].

In this model the defect accumulation process is viewed in terms of the development of a self-similar fractal cluster and the start of its avalanche-like growth as the appearance of macrocracks. In the opinion of the authors the fractal interpretation of fracture is used for the following reasons (confirmed by studies):

- under a load the surface of macrocracks possesses an irregular structure with different kinds of roughness being present;
- such a surface possesses relief self-similarity;
- self-similarity remains on the macro-, meso- and microlevels.

**Nanotechnologies** are related with the formation of nanoparticles with a high fraction of surface atoms whose physical-chemical characteristics differ considerably from those of atoms in the interior. In this connection nano-objects manifest dimensional effects and conditions are created for the following:

- self-organization and self-assembly, due to the high mobility of nano-particles and strong interatomic interaction; the role of the latter increases unabated as particle size decreases;



**Fig. 10.** Generalized dependence of the average sizes of a nanoparticle and fraction of atoms in the surface layer on the number of atoms in nanoparticles.

- creation of the prerequisites for non-standard nucleation of new phases and realization of phase transitions;
- manifestation of quantum effects;
- significant change of the kinetic coefficients of transport phenomena (diffusion, electricity and heat conduction, viscous flow).

It is noted in [3] that for different materials, properties and applications (even within the same material) size-dependent zones can lie in different dimensional ranges, for example, about 1 – 10 nm in chemistry and catalysis, about 1 – 100 nm in electronics and photonics and about 1 – 1000 nm in mechanics and magnetism. A number of silicate compounds (zeolite and others) and special glasses are used in these areas of science and technologies. The number of atoms in a nanoparticle, the dimensions of the particle and the fraction of surface atoms are all related with one another. Generalized relations are presented in Fig. 10. The diffuseness of the dependences is due to the effect of the kind and shape of nanoparticle on both characteristics. Usually, in nanochemistry (during catalysis) the criterion that the number of surface atoms equals the number of interior atoms is used for nanoparticles. As follows from Fig. 10, depending on a particle's type and shape the total number of atoms  $N \sim 10^3 - 10^5$  and the average particle size about 10 nm satisfy this criterion. The interrelation of nano-structural elements which are already formed in melts — clusters and

**TABLE 2.** Basic Technological Characteristics of Sheet Glass and Glass Container Manufacturing

Basic indicators	Indicator characteristics	
	Sheet glass	Glass containers
Glass article type	Simple (flat sheet)	Complex (cylindrical, conical, with special throat structure)
Glassmaking furnace	With developed convection	With limited convection and through flow
Forming preparations	Even cooling	Accelerated cooling (flow – channel – feeder)
Forming	Isothermal — on tin melt	Non-isothermal — press-and-blow in metal molds



fractals — can be seen in the implementation of nanotechnologies: a reduction of the number of atoms in nanoparticles results in the formation of spheroidal and then spherical nanoparticles with fractal structure owing to intensification of interatomic interactions.

The elements of nanotechnologies, some of which were implemented without special development, are used in glass manufacture. A characteristic example is colloidal coloring of decorative glasses, which has been known since ancient times. The conditions for self-organization of the coloring compounds (metal and nonmetal) into the corresponding clusters right up to the formation of crystal embryos are created in the glass melt. The rapid growth of viscosity during the forming of articles results in “self-freezing” of the high-temperature state together with the crystal embryos. Next, during additional heat-treatment (adjustments) the glass viscosity decreases, transport phenomena are activated, and conditions are created for growth of nanocrystals on embryos formed in the self-assembly regime [22].

In the second half of the 20th century size effects were already taken into account in the development of new materials and articles (sitals and photositals, photochromic and polychromic glass and others). Nanosize effects in combination with materials purity were already placed at the forefront on switching to a new generation of technologies (sol-gel, thin films, continuous colloidal coloring of float-glass, fiber light-guides and others).

Some examples of the implementation of nanotechnologies are presented in [4].

The presentation given above attests to the large amount of published information on silicate and glass melts. In recent years the number of publications in comparatively new directions in science — synergetics, fractals and nanotechnologies — has increased. These directions, and especially the first two, are related with the analysis of nonequilibrium systems, which silicate and glass melts are.

It should be noted that the application of methods of research and analysis of silicate systems in these directions are inadequate for purposeful comprehensive study of structural and technological particularities of glass melts.

For example, some researchers note that it is unclear whether glass comprises frozen melt or is a result of complex structure formation associated with the nucleation, growth and self-organization of non-crystalline clusters. Such a formulation is not entirely correct, because these concepts cannot be juxtaposed. Evidently, the process of self-organization of non-crystalline clusters can be viewed as the first stage of the process followed by self-freezing of the structure formed. At the same time F. Kh. Gaskell applied modern experimental-computational analysis to show that disordered (non-crystalline) clusters with fractal dimension 3D in the structure of medium range order are not seen for glasses whose composition is close to that of calcium metasilicate.

For this reason, scientific research on glass melts and the corresponding technological processes must be continued us-

ing modern methods in order to find solutions to the scientific and technological problems of the glass industry.

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